Journal of Hazardous Materials 307 (2016) 36–42

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

# Iron oxyhydroxide nanorods with high electrochemical reactivity as a sensitive and rapid determination platform for 4-chlorophenol

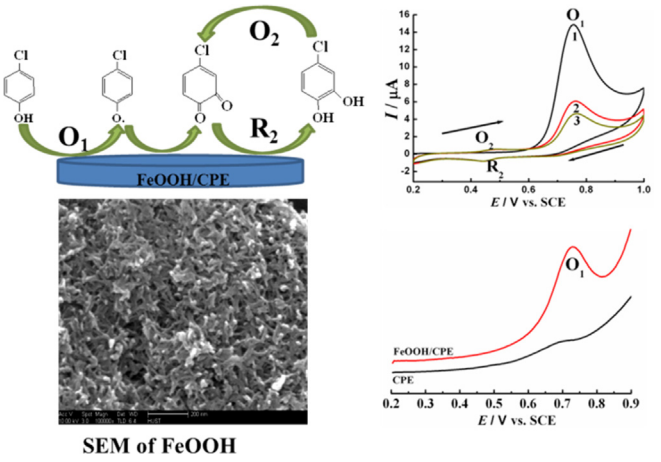
Yuanyuan Zhang[a,b], Qin Cheng[a], Meng Zheng[a], Xin Liu[b], Kangbing Wu[a,*]

[a] Key Laboratory for Material Chemistry of Energy Conversion and Storage, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] Britton Chance Center for Biomedical Photonics at Wuhan, National Laboratory for Optoelectronics-Hubei Bioinformatics & Molecular Imaging Key Laboratory, Systems Biology Theme, Department of Biomedical Engineering, College of Life Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

## HIGHLIGHTS

- Prepared FeOOH nanorods exhibited high reactivity toward the oxidation of 4-CP.
- Response signals and detection sensitivity of 4-CP increased greatly by FeOOH.
- Highly-sensitive and rapid determination platform was developed for 4-CP.
- Practical application in water samples was studied, and the accuracy was good.

## GRAPHICAL ABSTRACT




SEM of FeOOH

## ARTICLE INFO

*Article history:*
Received 9 September 2015
Received in revised form 2 December 2015
Accepted 30 December 2015
Available online 4 January 2016

*Keywords:*
4-Chlorophenol
Rapid determination
Iron oxyhydroxide
Nanorods
Electrochemical sensing

## ABSTRACT

Iron oxyhydroxide (FeOOH) nanorods were prepared through solvothermal reaction, and characterized using Raman spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, transmission electron microscopy and scanning electron microscopy. Thereafter, the prepared FeOOH nanorods were used as sensing material to construct a novel detection platform for 4-chlorophenol (4-CP). The electrochemical behaviors of 4-CP were studied, and the oxidation peak currents increased greatly on the surface of FeOOH nanorods. The signal enhancement mechanism was studied for 4-CP, and it was found that the prepared FeOOH nanorods remarkably improved the electron transfer ability and surface adsorption efficiency of 4-CP. The influences of pH value, amount of FeOOH nanorods and accumulation time were examined. As a result, a highly-sensitive electrochemical method was developed for the rapid determination of 4-CP. The linear range was from 10 to 500 nM, and the detection limit was 3.2 nM. It was used in different water samples, and the results consisted with the values that obtained by high-performance liquid chromatography.



## 1. Introduction

Chlorophenol isomers including 2-chlorophenol (2-CP), 3-chlorophenol (3-CP) and 4-chlorophenol (4-CP) have been widely

* Corresponding author. Fax: +86 27 87543632.
*E-mail address:* kbwu@hust.edu.cn (K. Wu).

http://dx.doi.org/10.1016/j.jhazmat.2015.12.064
0304-3894/

used as herbicides, fungicides, insecticides and intermediates in the production of pharmaceuticals and dyes [1]. They are a major group of pollutants of environmental concern because of their high toxicities [2]. Currently, the pollution of 4-CP is a major health concern because of its high endocrine disrupting potency, genotoxicity and wide existence [3,4]. The United States Environmental Protection Agency (USEPA) has listed 4-CP as one of the priority pollutants. Therefore, it is quite important to develop simple, rapid and sensitive methods for the determination of 4-CP. Until now, various techniques such as high-performance liquid chromatography (HPLC) [5], gas chromatography (GC) [6], spectrophotometry [7] and gas chromatography–mass spectrometry (GC–MS) [8] have been reported for the detection of 4-CP.

Due to the unique properties such as handling convenience, rapidness, high sensitivity, automatics and low cost, electrochemical determination has gathered increasing attention in the environmental monitoring. Up-to-date, various types of electrode materials, including cetyltrimethylammonium bromide functionalized-montmorillonite (CTAB-MMT) [9], mesoporous $TiO_2$ [10], nano-porous hydroxyapatite (HAp) [11], $Ni(OH)_2$ nanoparticles and carbon nanotubes composites ($Ni(OH)_2$–CNTs) [12] and three-dimensionally ordered macroporous (3-DOM) polycysteine [13], have been developed for the determination of 4-CP.

Iron oxyhydroxide (FeOOH) with excellent physical and chemical properties have been extensively studied, and obtained wide applications in the fields of energy storage and conversion [14,15], adsorbents [16,17] and electrochemical sensing [18]. Now, a number of methods have been developed for the preparation of FeOOH nanorods [19–22]. Herein, a kind of nanostructured iron oxyhydroxides was prepared *via* solvothermal reaction using iron (III) nitrate as the precursor and ethylene glycol as the solvent. The resulting FeOOH nanorods were then used to modify the carbon paste electrode (CPE), constructing a highly-sensitive electrochemical sensing platform for 4-CP. On the surface of FeOOH nanorods-modified CPE (FeOOH/CPE), the electron transfer ability and the accumulation efficiency of 4-CP increase obviously, and consequently, the oxidation signals of 4-CP enhance greatly. The greatly-increased response signals manifest that the prepared FeOOH nanorods are very sensitive for the determination of 4-CP. Compared with other reported electrochemical methods that listed in Table 1, we clearly find that this new determination platform for 4-CP possesses lower detection limit.

## 2. Experimental

### 2.1. Reagents

All chemicals were of analytical grade and used as received. 4-CP was purchased from the Sinopharm Group Chemical Reagent Co., Ltd., China, and dissolved into ethanol to prepare 0.01 M standard solution. Ethylene glycol (EG), polyethylene glycol 2000 (PEG), $Fe(NO_3)_3{\cdot}9H_2O$, $NH_4Ac$, graphite powder (spectral reagent) and paraffin oil were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). A series of phosphate buffer solutions with different pH values were prepared by mixing 0.1 M $NaH_2PO_4$ and 0.1 M $Na_2HPO_4$, and then adjusting the pH with 1.0 M $H_3PO_4$ or 1.0 M NaOH. Ultrapure water (18.2 MΩ) was obtained from a Milli-Q water purification system and used throughout.

### 2.2. Instruments

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Chenhua Instrument, Shanghai, China). A conventional three-electrode system, consisting of a carbon paste working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed. Scanning electron microscopy (SEM) characterization was conducted with a Quanta 200 microscope (FEI Company, Netherlands). Transmission electron microscopy (TEM) image was measured using a Tecnai G220 microscope (FEI Company, Netherlands). Raman spectra were acquired on a LabRAM HR800 confocal Raman microscopy using 532 nm laser (Horiba Jobin Yvon, France). X-ray diffraction (XRD) patterns were measured using an X'Pert PRO diffractometer (PANalytical B.V. Company, Netherlands). The energy dispersive X-ray spectroscopy (EDX) analysis was performed using a Quanta 200 microscope, and the prepared samples were dispersed on the C substrate.

High-performance liquid chromatography (HPLC) detection of 4-CP was carried out with Agilent 1100, coupled with a UV–vis detector. The C18 analytical column (4.6 mm × 150 mm × 5 μm) was used. The mobile phase was acetate buffer containing 5 mM ammonium acetate and acetic acid (A), acetonitrile (B) and methanol (C), filtered through 0.45-μm Millipore filter prior to use. The isocratic elution was programmed as 65% A, 28% B and 7% C. The flow rate was 1 mL $min^{-1}$, and the sample injection volume was 100 μL. The detection wavelengths were 227 nm for 4-CP.

### 2.3. Preparation of FeOOH/CPE

The used FeOOH nanorods were prepared through solvothermal method. Firstly, 12.5 mmol $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved into 150.0 mL EG to form a clear solution, and 7.5 g PEG and 125.0 mmol $NH_4Ac$ were then added. After 2-h vigorous stirring, the mixture was sealed in a Teflon-lined stainless-steel autoclave, and reacted for 24 h at 160 °C. After being cooled to room temperature, the brown products were washed several times with ethanol and water, and finally dried at 80 °C for 12 h.

After that, 0.15 g of the obtained FeOOH solid samples were mixed with 0.85 g graphite powder in a carnelian mortar. The total mass was controlled at 1.00 g and the mass content of FeOOH was 15%. After that, 0.30 mL paraffin oil was added, and then mixed homogeneously. The resulting carbon paste was tightly pressed into the end cavity (3.0 mm in diameter, 1.0 mm in depth) of a Teflon holder in which electrical contact was made with a copper rod that runs through the center of the electrode body. Finally, the electrode surface was polished on a smooth paper. The unmodified CPE was prepared as above procedure, only using 1.00 g graphite powder and 0.30 mL paraffin oil.

**Table 1**
Performance comparison of electrochemical methods for the determination of 4-CP.

| Electrode materials | Linear range (nM) | Detection limit (nM) | Accumulation time (min) | Ref. |
|---|---|---|---|---|
| CTAB-MMT | 50–$1 \times 10^4$ | 20 | 2 | [9] |
| Mesoporous $TiO_2$ | 50–$5 \times 10^4$ | 10 | 3 | [10] |
| Porous HAp | 10–100 | 4.0 | 4 | [11] |
| $Ni(OH)_2$–CNTs | 1000–$7.5 \times 10^5$ | 500 | 2 | [12] |
| 3-DOM polycysteine | 50–3000 | 17 | 2 | [13] |
| FeOOH nanorods | 10–500 | 3.2 | 2 | This work |